CHAPTER I
INTRODUCTION
INTRODUCTION

Catalysis research is central to the science of modern chemical processing, fuel technologies and environmental control. It controls more than 90% of the world’s chemical manufacturing processes and is one of the most important technologies in national economics. Research into catalysis is a major field in applied science, and involves many fields of chemistry and physics. Modern society as we know it would be impossible without catalysis.

Industrial production of chemicals can be categorized into several distinct branches. Petrochemicals, large-volume organic chemicals and monomers are products of bulk chemicals. Advanced intermediates, pesticides, active ingredients, vitamins, flavour and fragrance chemicals are produced by the fine chemical industry. The production of pharmaceuticals is often considered a part of the latter branch but, in view of importance, can also be seen as a separate part of the chemical industry. Table 1 lists the respective plant scales of these three branches. Although the total production in weight of fine chemicals is considerably less than that of bulk chemicals, its economic impact is huge. Whereas the bulk chemical industry has replaced environmentally unacceptable processes by cleaner catalytic alternatives, production of fine chemicals is still hampered by early twentieth century technologies using stoichiometric amounts of acids, bases or oxidants. Due to this, every kg of product in the fine chemical industry is accompanied by on average 15 - 20 kg of waste, which may cause environmental damage (Table 1). Therefore, major efforts have to be
undertaken to comply with present and future legislation to diminish these waste streams. Thus, current research has to focus on the development of cleaner alternatives.

**Table 1 Estimated production of chemicals**

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Plant scale (t/a)</th>
<th>kg by-product/kg product (E factor)</th>
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<tbody>
<tr>
<td>Bulk chemicals</td>
<td>$10^4$-$10^6$</td>
<td>&lt;1 to 5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^2$-$10^4$</td>
<td>5 to 50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10$-$10^3$</td>
<td>25 to &gt;100</td>
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</tbody>
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**Homogeneous catalysis**

In homogeneous catalysis, the reactants, products and catalyst are all in the same phase usually liquid phase. Often the reactants, products and catalyst are all dissolved in the same solvent. Advantages of homogeneous catalysts are their high specificity and generally low temperature and pressure requirement. Specificity is possible because the catalytic behavior of a particular metal complex can be subtly altered by varying the ligands, co-ordination number of complex or the oxidation state of the central metal atom.

The main disadvantages of the homogeneous catalysts are the difficulty in separating the catalyst from the product, degradation of the catalyst and the high initial cost especially if noble metals are required.
Heterogeneous Catalysis

Catalysts, which operate on reactions taking place on surfaces, heterogeneous catalysts, are of great importance in chemical industry and in living organisms. In heterogeneous catalysis, the reacting species are held on the surface of the catalyst by a physical attraction called adsorption while the reaction takes place. Adsorption may be relatively weak (physical adsorption) or may have strength comparable to the strengths of chemical bonds (chemisorption). In either case adsorption is generally not uniform across a solid surface. Adsorption, and therefore catalysis, occurs primarily at certain favorable locations called active sites.

Eg: The industrial synthesis of ammonia requires solid catalysts in order to obtain reasonable rates of reaction. The overall mechanism, including the adsorption steps, is believed to be:

1. $\text{N}_2 (g) \rightarrow \text{N}_2 (\text{ads})$
2. $\text{N}_2 (\text{ads}) \rightarrow 2\text{N} (\text{ads})$
3. $\text{H}_2 (g) \rightarrow \text{H}_2 (\text{ads})$
4. $\text{H}_2 (\text{ads}) \rightarrow 2\text{H} (\text{ads})$
5. $\text{N} (\text{ads}) + 3\text{H} (\text{ads}) \rightarrow \text{NH}_3 (\text{ads})$
6. $\text{NH}_3 (\text{ads}) \rightarrow \text{NH}_3 (g)$
How does a heterogeneous catalyst work?

A reaction catalyzed by a heterogeneous catalyst can be represented by a flow chart shown below (Figure 2).

Step 1 reactant + catalyst  Step 2 reactant/catalyst complex

Step 3 product/catalyst complex  Step 4 product + catalyst

Figure 2. Synthesis of ethane from ethene using a heterogeneous nickel catalyst
Making and breaking bonds

Reactant molecules are adsorbed at active sites onto the surface of the catalyst. This involves the formation of weak bonds between reactant molecules and the catalyst, which causes other bonds in the reactant molecule to be stretched and weakened. The weakened structure is converted to another complex that is essentially the product attached to the catalyst. Finally, this complex breaks down to release the product molecule, which moves away to leave the catalyst surface ready to with another reactant molecule.

Some of the important catalytic processes include:

- The Haber process for ammonia synthesis
- Steam reforming of hydrocarbons to produce synthesis gas
- Fischer-Tropsch synthesis
- Hydrogenation/dehydrogenation of organic compounds
- Petroleum refining and processing
- Hydrotreating - hydrogenation of hydrocarbons and removal of organic sulfur, nitrogen, oxygen, and metals
- Industrial and automotive abatement of NOx, CO, and hydrocarbons
- Nearly every chemical process associated with life.
Table 2. Strong and weak points of homogeneous and heterogeneous catalysts

<table>
<thead>
<tr>
<th></th>
<th>Homogeneous</th>
<th>Heterogeneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong points</td>
<td>defined on molecular level, Separation, recovery, scope, variability (design)</td>
<td>handling, stability, re-use</td>
</tr>
<tr>
<td></td>
<td>(availability)</td>
<td></td>
</tr>
<tr>
<td>Weak points</td>
<td>sensitivity, activity, productivity (separation)</td>
<td>Characterization, reproducibility, availability, preparation, narrow scope</td>
</tr>
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Polymer

A substance, which is composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent bonds.

Usually, a molecule is considered to be macromolecular when it exhibits properties typical of high molecular weight substances. Monomer molecules by linking with together through a chemical reaction forms macromolecules. The process by which this is achieved being known as polymerization.

Linear polymers may be represented by a chain with two ends.

Branched polymers have side chains, or branches, of significant length, which are bonded to the main chain at branch points, and are characterized in terms of the number
and size of the branches. Polymers with well-controlled modes of branching: comblike polymers, star polymers, dendrimers, etc.

Network polymers have three-dimensional structures in which each chain is connected to all others, and are characterized by their crosslinking density or degree of crosslinking (number of junction points per unit volume) (Figure 3).

![Linear Branched Network](image)

**Figure 3. General structure of various polymers**

**Polymer supported catalysts**

Organometallic catalysts are often tethered to cross-linked polymers such as polystyrene in order to recover the catalyst by simple filtration and reuse it. Often, it has been observed that the activity of the catalyst is reduced in these systems. If the catalyst is enantioselective, then poor stereoselectivity is observed when the catalyst is supported on polymers with poor solubility. In recent years, it has been shown that if the catalyst is tethered to a soluble polymer, then the catalytic activity is maintained. To recover the catalyst, a secondary solvent is added to 'precipitate' the polymer. However, this often requires large amount of the solvent. The challenge is to develop methods for the easy recovery of soluble polymer supported catalysts.
Different types of polymer supported catalysts

The main kinds of polymeric or polymer supported catalysts are

1. Ion exchange resin catalysts
2. Insoluble polymer-supported catalysts
3. Soluble polymer-supported catalysts

I. Ion exchange resin catalysts

An ion-exchange resin is an insoluble matrix (or support structure) normally in the form of small (1-2 mm diameter) beads, fabricated from an organic polymer substrate on the surface of which are sites with easily trapped and released ions in a process called ion exchange.

There are multiple different types of ion exchange resins, which are fabricated to selectively prefer one or several different types of ions.

There are four main types differing in their functional groups:

- Strongly acidic (sulfonic acid groups)
- Strongly basic, (trimethylammonium groups)
- Weakly acidic (carboxylic acid groups)
- Weakly basic (amino groups)

Applications of resin catalysts

1. Alkylation

Phenol reacts with branched olefins to give phenol alkylate over a dry macroporous strong acid resin at 120 to 150 °C.
2. Esterification

The direct esterification of alcohol with organic acid is for the production of esters by strong acid resin, replacing sulfuric acid.

3. Aldol condensation

Condensation of acetone to diacetone alcohol can be catalyzed by macroporous weak base or strong base anion, replacing sodium hydroxide with conversion 90-95% at 55 °C.

II. Soluble polymer-supported catalysts

Soluble polymer supported catalyst must have the following specifications:

➢ To combine the principal beneficial features of heterogeneous and homogeneous systems.

➢ To achieve catalyst recovery without the polymer affecting the chemistry of solution phase process.

➢ Soluble polymer-supported catalysts were prepared by grafting ligand and metal complex on polymer.

Ex: Poly(acrylic acid salt)- supported chiral ruthenium complex catalyst was prepared by bonding the chiral diimino-diphosphine ligand on the polymer with trans-Ru complex.

III. Insoluble polymer-supported catalysts

There are two methods to prepare insoluble polymer-supported catalysts by grafting or bonding active sites:
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1. To select the polymeric substrate with functional groups, based on catalyst components.

Ex: Immobilized chiral rhodium catalyst was prepared by grafting dirhodium(II) carboxamidates on polystyrene-polyethylene glycol copolymer.

2. To select the polymeric substrate based on polarities of reactants and then functionalize it based on catalyst components.

Ex: Polymer-encapsulated Pd/C catalyst was prepared by dispersing Pd on carbon in POEPOP copolymer.

➢ It was used in solution phase hydrogenation of a double and a triple bond as well as hydrogenolysis of a benzyl protecting group.

➢ Its reactivity is nearly close to standard 10 % Pd/C.

➢ It shows a better stability for reuse without significant loss of reactivity.

Advantages of performing chemistry either on polymer supports, or with polymer-supported reagents or catalysts

A. Cleaner methods

Cross-linked polymers are insoluble and non-volatile, they are odourless and non-toxic and are therefore more environmentally friendly. Highly toxic chemicals can be rendered inert and harmless through attachment to a polymer support - no toxic materials can be released to the atmosphere. A move towards clean technologies has been noted as a key area of importance by the government Foresight committee. The
current cost of waste disposal is higher than the original cost of starting materials and chemicals.

B. Potential for automated synthesis and testing using high-throughput screens

Polymer-supported chemistry readily lends itself to the development of automated techniques. Automated (robotic) methods are already known and are becoming increasingly used by industry. For polymer-supported catalysts the possibility exists to develop both insoluble and soluble polymer derivatives - insoluble catalysts have the advantage that they can be removed by filtration, allowing rapid re-cycling for re-use. With soluble polymers the catalysis takes place in an homogenous medium which may be beneficial to a particular reaction, the catalysts may ultimately be rendered insoluble for re-isolation by precipitation.

C. Simplified product isolation and recovery

After completion of a reaction, the desired target and the insoluble polymer-supported reagent can be separated simply by filtration of the insoluble polymer support. In the case of polymer-supported catalysts, this would enable quantitative re-isolation for re-use, therefore increasing efficiency. For polymer-supported reagents the resulting by-product would remain attached to the polymer-support. In either case, the need for tedious, and sometimes low yielding, purification and re-isolation methods is removed.

Biopolymers

Biopolymers are large molecules made of repeating units. These molecules generally are available in abundance from natural sources, have little or no toxicity, and
are water soluble in certain molecular weight ranges. Examples of biopolymers are polyamino acids, proteins, polysaccharides, and oligonucleotides.

Biopolymers are polymers that are biodegradable. The input materials for the production of these polymers may be either renewable (based on agricultural plant or animal products) or synthetic. There are four main types of biopolymer based respectively on:

1. Starch
2. Sugar
3. Synthetic materials
4. Cellulose

Current and future developments in biodegradable polymers and renewable input materials focus relate mainly to the scaling-up of production and improvement of product properties. Larger scale production will increase availability and reduce prices.

These biopolymers have properties that make them suitable for use in protecting products from moisture, increasing shelf-life and making products easier to dispense. Every biopolymer has its own material-specific properties, e.g. barrier properties such as oxygen permeability. The barrier properties are relevant to the choice of biopolymers for the packaging of particular products. Bioplastics have very promising prospects for use in pesticide soil pins, for packaging in-flight catering products and for packaging dairy products.
1. Starch based polymers

Sources

Starch is a natural polymer, which occurs as granules in plant tissue, from which it can easily be recovered in large quantities. It is obtained from potatoes, maize, wheat and tapioca and similar sources. Starch can be modified in such a way that it can be melted and deformed thermoplastically. The resulting material is thus suitable for conventional plastic forming processes such as injection moulding and extruding.

Applications

It has good oxygen barrier properties.

2. Sugar based biopolymers

Sources

The starting material for polyhydroxybutyrate is made from sucrose or starch by a process of bacterial fermentation. Varying the nutrient composition of the bacteria produces differences in the end product. This makes it possible to tune the properties of the material, e.g. its moisture resistance. The polymer can be formed by injection, extrusion, blowing and vacuum forming.

Polylactides (lactic acid polymers) are made from lactic acid, which is in turn made from lactose (or milk sugar) obtained from sugar beet, potatoes, wheat, maize etc. Polylactides are water resistant and can be formed by injection moulding, blowing and vacuum forming.

Applications

Polylactides decompose harmlessly in the human body and have therefore long been
used for medical applications. Examples include surgical implants, which do not require operative removal.

3. Synthetic based biopolymers

Sources

Synthetic compounds derived from petroleum can also be a starting point for biodegradable polymers, e.g. aliphatic aromatic copolyesters. These polymers have technical properties resembling those of polyethylene (LDPE). Although these polymers are produced from synthetic starting materials, they are fully biodegradable and compostable.

Applications

The best known application is for making substrate mats.

4. Cellulose based biopolymers

Sources

The use of cellulose for making packaging material such as cellophane is long established. The material is transparent and has good folding properties. Whether in the form of pure cellulose or of a nitrocellulose coating, the material is wholly biodegradable and can be composted by existing waste processing plant.

Conventional plastics are often seen as environmentally unfriendly. Sustainable plastics could therefore provide an image advantage.

The major advantage of biodegradable packaging is that it can be composted. But the biodegradability of raw materials does not necessarily mean that the product or package made from them (e.g. coated paper) is itself compostable.
Applications

Familiar applications of cellophane include packaging for CDs, confectionary and cigarettes. The material is gradually falling out of favour, however, owing to its high price (about US$6 per kilogram). Other cellulose polymer materials (e.g. cellulose film) have also been commercially available for many years but are losing market share to newer polymers such as polypropylene.

Cellulose

The existence of cellulose as the common material of plant cell walls was first recognized by Anselm Payen in 1838. It occurs in almost pure form in cotton fiber and in combination with other materials, such as lignin and hemicelluloses, in wood, plant leaves and stalks, etc. Although generally considered a plant material, cellulose is also produced by some bacteria.

It has been accepted for many years that cellulose is a long chain polymer, made up of repeating units of glucose, a simple sugar. In the early 1900s, cellulose was further characterized by Cross and Bevan. They removed the related plant materials that occur in combination with cellulose by dissolving them in a concentrated sodium hydroxide solution. They designated the undissolved residue as α-cellulose. The soluble materials (designated as β-cellulose and γ-cellulose) were later shown not to be celluloses, but rather, relatively simple sugars and other carbohydrates. The α-cellulose of Cross and Bevan is what is usually meant when the term “cellulose” is used now.
As a carbohydrate, the chemistry of cellulose is primarily the chemistry of alcohols and it forms many of the common derivatives of alcohols, such as esters, ethers, etc. These derivatives form the basis for much of the industrial technology of cellulose in use today. Because of the strong hydrogen bonds that occur between cellulose chains, cellulose does not melt or dissolve in common solvents. Thus, it is difficult to convert the short fibers from wood pulp into the continuous filaments needed for artificial silk, an early goal of cellulose chemistry. Several different cellulose derivatives were examined as early routes to artificial silk, but only two, the acetate and xanthate esters, are of commercial importance for fibers today. Cellulose derivatives are used commercially in two ways, as transient intermediates or as permanent products.

Cellulose acetate is soluble in organic solvents such as acetone and can be spun into fiber or formed into other shapes. Xanthate esters are formed when cellulose is first treated with strong alkali and then exposed to carbon disulfide. Cellulose xanthate is soluble in aqueous alkali; and the resulting solution can be extruded as filaments or films. This is the basis for the viscose process for rayon manufacture.

The Chemistry of Cellulose

In the cellulose chain, the glucose units are in 6-membered rings, called pyranoses(Figure 4). They are joined by single oxygen atoms (acetal linkages) between the C-1 of one pyranose ring and the C-4 of the next ring. Since a molecule of water is lost when an alcohol and a hemiacetal react to form an acetal, the glucose units in the cellulose polymer are referred to as anhydroglucose units.
The spatial arrangement, or stereochemistry, of these acetal linkages is very important. The pyranose rings of the cellulose molecule have all of the groups larger than hydrogen sticking out from the periphery of the rings (equitorial positions). The stereochemistry at carbons 2, 3, 4 and 5 of of the glucose molecule are fixed; but when glucose forms a pyranose ring, the hydroxyl at C-4 can approach the carbonyl at C-1 from either side, resulting in two different stereochemistries at C-1.

![Diagram of cellulose structure]

**Figure 4. General structure of Cellulose**

When the hydroxyl group at C-1 is on the same side of the ring as the C-6 carbon, it is said to be in the α configuration (not to be confused with α-cellulose, which is not related). In cellulose, the C-1 oxygen is in the opposite, or β configuration (*i.e.*, cellulose is poly[β-1,4-D-anhydroglucopyranose]).
This β configuration, with all functional groups in equatorial positions, causes the molecular chain of cellulose to extend in a more-or-less straight line, making it a good fiber-forming polymer.

Because of the equatorial positions of the hydroxyls on the cellulose chain, they protrude laterally along the extended molecule. This positioning makes them readily available for hydrogen bonding. These hydrogen bonds cause the chains to group together in highly ordered (crystal-like) structures. Since the chains are usually longer than the crystalline regions, they are thought to pass through several different crystalline regions, with areas of disorder in between (the “fringed-micelle” model). The inter-chain hydrogen bonds in the crystalline regions are strong, giving the resultant fibers good strength and insolubility in most solvents. They also prevent cellulose from melting (i.e., non-thermoplastic). In the less ordered regions, the chains are further apart and more available for hydrogen bonding to other molecules, such as water. Most cellulose structures can absorb large quantities of water (i.e., it is very hygroscopic). Thus, cellulose swells, but does not dissolve, in water.

Figure 5 presents the four different pathways cellulose is accessed today. As described above, the pathway is the production of cellulose from plants, the seed hairs of cotton, cellulose is available in almost pure form. In contrast, wood cellulose forms a native composite material with lignin and other polysaccharides (hemicelluloses) from which it is isolated by large-scale chemical pulping, separation, and purification processes.
Apart from plants, certain bacteria, algae, and fungi produce cellulose as well. Because of their specific supramolecular structures, these cellulose forms are frequently used as model substances for further research on cellulose structure, crystallinity, and reactivity, as well as for the development of new materials and biomaterials (Section 6). On this basis, the biosynthesis of cellulose has been investigated in detail over the past decades. Therefore, it is known that the biosynthesis of cellulose has been part of the life cycle of cyanobacteria for over 3.5 billion years. The synthesis of cellulose in vitro should be highlighted as an additional important development in recent years.

Figure 5. Principle pathways to cellulose formation
Zeolites

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminum, silicon, and oxygen in their regular framework; cations and water are located in the pores. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen atoms. Zeolites are natural minerals that are mined in many parts of the world; most zeolites used commercially are produced synthetically. Zeolites have void space (cavities or channels) that can host cations, water, or other molecules. Because of their regular and reproducible structure, they behave in a predictable fashion. Zeolites are available as powders or as formed products such as extrudates. Zeolites, like other solids, are safe to handle and are easy to use in a variety of reactors.

Discovery of zeolites

In 1756, the Swedish mineralogist Axel Fredrick Cronstedt discovered that stilbite, a natural mineral, visibly lost water when heated, and he named the class of materials zeolites from the classical Greek words meaning 'boiling stones.' Zeolites were considered an obscure group of minerals with unique properties for almost 200 years, and Cronstedt was remembered primarily for discovering the element nickel.

Applications for zeolites

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as
traps for molecules so they can be analyzed, or as catalysts by confining molecules in small spaces, which causes changes in their structure and reactivity.

Zeolites can be used as solar thermal collectors and for adsorption refrigeration.

**Adsorption and Ion Exchange**

Zeolites are used to adsorb a variety of materials. This includes applications in drying, purification, and separation. They can remove water to very low partial pressures and are very effective desiccants, with a capacity of up to more than 25% of their weight in water. They can remove volatile organic chemicals from air streams, separate isomers and mixtures of gases [11-15].

The largest volume use for zeolites is in detergent formulations where they have replaced phosphates as water-softening agents. They do this by exchanging the sodium in the zeolite for the calcium and magnesium present in the water.

**How do zeolites function as ion exchangers?**

The framework aluminum and silicon are bound to each other through shared oxygen atoms. The SiO$_4$ units are neutral: Si$^{+4}$/4O$^{-}$ but the AlO$_4$ results in a net negative charge: Al$^{+3}$/4O$^{-}$. The net negative charge is balanced by cations that are present during the synthesis. These cations are highly mobile and can be exchanged for other cationic species.

**Catalysis**

Zeolites can be shape-selective catalysts either by transition state selectivity or by exclusion of competing reactants on the basis of molecular diameter. Zeolites can also be acid catalysts and can be used as supports for active metals or reagents [16-20].
They have also been used as oxidation catalysts. The main industrial application areas are: petroleum refining, synfuels production, and petrochemical production. Synthetic zeolites are the most important catalysts in petrochemical refineries.

Types of zeolites

There are numerous naturally occurring and synthetic zeolites, each with a unique structure. The pore sizes commercially available range from approximately 3 Å to approximately 8 Å. Some of the commercial materials are: zeolite A, zeolite beta, mordenite, zeolite Y, ZSM-5.

Re-usability of zeolites

Zeolites can be regenerated using relatively easy methods such as heating to remove adsorbed materials, ion exchanging with sodium to remove cations, or pressure swing to remove adsorbed gases.

Modification of zeolites

Zeolite modification implies an irreversible change, unlike ion exchange or adsorption. There are a number of different ways that zeolites can be modified. The framework of the zeolite can be modified by synthesizing zeolites with metal cations other than aluminum and silicon in the framework. The framework of the zeolites can be modified by dealumination to increase the silica and increase the hydrophobic nature of the zeolite. There are many proprietary methods to modify zeolites that impart unique characteristics to them.
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Preparation of synthetic zeolites

During the 1930's, R. Barrer and J. Sameshima did extensive work in zeolite synthesis. In 1948, Richard Barrer first produced a synthetic zeolite that did not have a natural counterpart. At approximately the same time, Milton made the first materials that had no natural counterpart such as zeolite A. There are several types of synthetic zeolites that form by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates.

Speciality of zeolites when compared with other inorganic oxide materials

The combination of many properties, among them: the microporous character of the uniform pore dimensions, the ion exchange properties, the ability to develop internal acidity, the high thermal stability, the high internal surface area. These make zeolites unique among inorganic oxides.

Since many biological processes are related to properties exhibited by zeolites, these materials have also been studied and used in the medical field recently. Their biological activity has been tested in anticancer therapy and for the treatment of diarrhoea [21].

Zeolite beta

Beta zeolite is an old zeolite discovered before Mobil began the "ZSM" naming sequence. As the name implies, it was the second in an earlier sequence. The structure of zeolite beta was only recently determined because the structure is very complex and interest was not high until the material became important for some dewaxing
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operations. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A and B. [Figure 6, (a) and (b)]

![Beta-Polymorph A](image1.png)

![Beta-Polymorph B](image2.png)

(a) Beta-Polymorph A  
(b) Beta-Polymorph B

Figure 6. Distinct structures of zeolite beta

The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The intergrowth of the polymorphs does not significantly affect the pores in two of the dimensions, but in the direction of the faulting, the pore becomes tortuous, but not blocked. The two hypothetical polymorphs are depicted here. The projection view of zeolite beta along [100] plane is as shown in the figure below.

![Projection view of zeolite beta along [100] plane](image3.png)

Figure 7. Projection view of zeolite beta along [100] plane
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Genesis of present work

The recent developments in heterogeneous catalysis in various organic transformations prompted us to develop new catalysts using cellulose biopolymer as a support and to try these catalysts for different reactions. The cellulose supported Copper(0) catalyst [CELL-Cu(0)] is an effective catalyst for N-arylation of nitrogen heterocycles with aryl halides and aryl boronic acids to afford N-aryl heterocycles in excellent yields. The same catalyst [CELL-Cu(0)] is also used for aza-Michael addition of N-nucleophiles such as amines and imidazoles to α, β-unsaturated compounds with low catalyst loading than earlier to afford the aza-Michael adducts in excellent yields.

The cellulose supported palladium(0) [CELL-Pd(0)] is found to be highly active for well-known C-C bond forming reactions such as Heck reaction of various olefins with aryl iodides and Sonogashira coupling of phenyl acetylene with different aryl halides and afforded good to excellent yields. Thus the chapters II-IV deals with the synthesis, characterization of cellulose supported catalysts and their applications in various organic reactions. These cellulose supported palladium and copper catalysts were reused for several cycles.

Zeolite beta is found to be an efficient and eco-friendly catalyst for the nitration of o-xylene with high regio-selectivity in liquid phase conditions. Chapter V deals with the optimization of the reaction conditions for the nitration of o-xylene such as effect of solvent, temperature, etc.

All the catalysts were well characterized by various instrumental techniques. All the catalysts were recyclable and are truly heterogeneous.
Conclusions and Outlook

The metal supported catalysis is a fascinating topic and currently several research groups both in industries and universities are active in this area. There are many examples demonstrating the efficient separation by filtration or sedimentation. In a few cases, re-use of the recovered catalyst is possible without loss of performance. These catalysts can be applied in continuous flow reactors. This technique has advantages in cases where a high concentration of catalyst is required to obtain good selectivities or where degradation of the support particle by stirring is a problem. Also, in a few cases, catalytic properties could be improved by the effect of site isolation or by tuning the surroundings of the catalyst.

Cellulose and its derivatives are widely used in chemical and bio-chemical applications and also as supports for the synthesis of organic molecules. It is also observed that cellulose fibers act as nanoreactor for the stabilization of metal nanoparticles. Cellulose and modified cellulosic materials can be used as sorbents for metal ions from aqueous solutions. In particular, the exciting developments in selective catalysis by cellulose or its derivatives as supports will undoubtedly find widespread application in the synthesis of fine and speciality chemicals. The implementation of "clean catalytic technologies" will play an important role in the much-needed reduction of waste in the industry segment.
References


187.